Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Vapor Transport

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Interest in optical devices which can operate in the visible spectrum has motivated research interest in the II-VI wide band gap semiconductor materials. The recent challenge for semiconductor optoelectronics is the development of a laser which can operate at short visible wavelengths. In the past several years, major advances in thin film technology such as molecular beam epitaxy and metal organic chemical vapor deposition have demonstrated the applicability of II-VI materials to important devices such as light-emitting diodes, lasers, and ultraviolet detectors. With an energy gap of 2.7 eV at room temperature, and an efficient band-to-band transition, ZnSe has been studied extensively as the primary candidate for a blue light emitting diode for optical displays, high density recording, and military communications. By employing a ternary or quaternary system, the energy band gap of II-VI materials can be tuned to a specific range. While issues related to the compositional inhomogeneity and defect incorporation are still to be fully resolved, ZnSe bulk crystals and ZnSe-based heterostructures such as ZnSe/ZnSeS, ZnSe/ZnCdSe and ZnCdSe/ZnSeS have showed photopumped lasing capability in the blue-green region at a low threshold power and high temperatures. The demonstration of its optical bistable properties in bulk and thin film forms also make ZnSe a possible candidate material for the building blocks of a digital optical computer. Despite this, developments in the crystal growth of bulk II-VI semiconductor materials has not advanced far enough to provide the low price, high quality substrates needed for the thin film growth technology.

The electrical and optical properties of semiconductor materials depend on the native point defects (the deviation from stoichiometry) and the impurity or dopant distribution. To date, the bulk growth of ZnSe substrates has been plagued with problems related to defects such as non-uniform distributions of native defects, impurities and dopants, lattice strain, dislocations, grain boundaries, and second phase inclusions, which greatly effect the device performance. In the bulk crystal growth of some technologically important semiconductors, such as ZnTe, CdS, ZnSe, and ZnS, vapor growth techniques have significant advantages over melt growth techniques due to the high melting points of these materials. The realization of routine production of high-quality single crystals of these semiconductors requires a fundamental, systematic and in-depth study on the PVT growth process and crystal growth by vapor transport in low gravity offers a set of unique conditions for this study.

Previously, two reasons have been put forward to account for this. The first is weight-related reductions in crystal strain and defects. These are thought to be caused by the weight of the crystals during processing at elevated temperatures and retained on cooling, particularly for materials with a low yield strength. The second, and more general, reason is related to the reduction in density-gradient driven convection. The PVT crystal growth process consists of essentially three processes: sublimation of the source material, transport of the vapor species, and condensation of the vapor species to form the crystal. The latter two processes can be affected by the convection caused by gravitational accelerations on Earth. Reductions in such convection in low gravity is expected to yield a nearly diffusion-limited growth condition, which results in more uniform growth rates (on the microscopic scale) and hence greater crystalline perfection and compositional homogeneity. The reduction of convective contamination by performing flight experiments in a reduced gravity environment will help to simplify the complexity of the coupled mass transport and growth kinetics problem. An improved comparison between the experimental results and theoretical simulations is also expected and will be beneficial to any growth process involving vapor mass transport or vapor-crystal interface growth kinetics.

The following are the scientific objectives of the proposed flight experiments, listed in order of priority:

- 1. Grow ZnSe crystals in reduced gravity using a seeded PVT process to:
 - Establish the relative contributions of gravity-driven fluid flows to: (a) the incorporation of impurities and defects; and, (b) the deviation from stoichiometry observed in the grown crystals as the result of buoyancy-driven convection, irregular fluid-flows and growth interface fluctuations.
 - Assess the amount of strain developed during processing at elevated temperatures and retained on cooling caused by the weight of the crystals.
 - Obtain a limited amount of high quality space-grown materials for various thermophysical and electrical properties measurements and as substrates for device fabrication and thus assess device performance as influenced by a substantial reduction in gravity-related effects.
- 2. Perform *in-situ*, real-time optical measurements during growth to independently determine:
 - The vapor concentration distribution by partial pressure measurements using optical absorption.
 - The evolution of growth interface morphology and instantaneous growth velocity by optical interferometry.
 - And thus help to simplify the complexity of the coupled mass transport and growth kinetics problem.
- 3. Evaluate the additional effects of gravity on the PVT process in the future flight experiments by:
 - Examining the dopant segregation and distribution in the Cr doped ZnSe.
 - Analyzing the compositional segregation and distribution in the ternary compounds grown by PVT.